AFWAL-TR-87-2042
Volume XVI

PRODUCTION OF JET FUELS FROM COAL DERIVED LIQUIDS

VOL XVI - Analysis of Phenolic Species in Coal Derived Aviation Fuels

F. D. Guffey
D. E. Hunter

WESTERN RESEARCH INSTITUTE
P O BOX 3395
UNIVERSITY STATION
LARAMIE, WYOMING 82071

JUNE 1990

INTERIM REPORT FOR THE PERIOD SEPTEMBER 1988 - JULY 1989

AERO PROPULSION AND POWER LABORATORY
WRIGHT RESEARCH AND DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligation whatsoever. The fact that the government may have formulated or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication, or otherwise in any manner construed, as licensing the holder, or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

WILLIAM E. HARRISON III
Fuels Branch
Fuels and Lubrication Division

CHARLES L. DELANEY, Chief
Fuels Branch
Fuels and Lubrication Division

FOR THE COMMANDER

LEO S. HAROOTYAN, JR., Assistant Chief
Fuels and Lubrication Division
Aero Propulsion and Power Laboratory

If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify WRDC/POSF, WPAFB, OH 45433-6563 to help us maintain a current mailing list.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY N/A	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution is unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-87-2042, Vol. XVI
6a. NAME OF PERFORMING ORGANIZATION Western Research Institute 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Aero Propulsion and Power Laboratory Wright Research & Development (WRDC/POSF)
6c. ADDRESS (City, State, and ZIP Code) P.O. Box 3395 University Station Laramie, WY 82071	7b. ADDRESS (City, State, and ZIP Code) Wright-Patterson AFB, OH 45463-6563
8a. NAME OF FUNDING/SPONSORING ORGANIZATION N/A 8b. OFFICE SYMBOL (If applicable) N/A	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER FY1455-86-N0657
8c. ADDRESS (City, State, and ZIP Code) N/A	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 63216F; PROJECT NO. 2480; TASK NO. 16; WORK UNIT ACCESSION NO. 01

11. TITLE (Include Security Classification)
Production of Jet Fuel from Coal Derived Liquids, Vol XVI - Analysis of Phenolic Species in Coal-Derived Aviation Fuels

12. PERSONAL AUTHOR(S)
F. D. Guffey and D. E. Hunter

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM 8809 TO 8907	June 1990	43

16. SUPPLEMENTARY NOTATION
None

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Jet Fuels, Coal Derived Jet Fuels, Coal, Coal Liquids, JP-4, JP-8, JP-8X, Oxygenates Fuel Properties, Fuel Composition, Stability

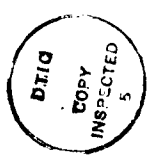
19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Samples of jet fuel (JP-4, JP-8, JP-8X) produced from the liquid by-products of the gasification of lignite coal from the Great Plains Gasification Plant were analyzed to determine the quantity and type of organo-oxygen compounds present. Large quantities of oxygen compounds were found in the coal derived liquids and were removed in the refining process. Trace quantities of organo-oxygenate compounds were suspected to be present in the refined fuels. Compounds were identified and quantified as part of an effort to determine the effect of these compounds in fuel instability.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL William E. Harrison III	22b. TELEPHONE (Include Area Code) 513-255-6601	22c. OFFICE SYMBOL WRDC/POSF

DD Form 1473, JUN 86 *Previous editions are obsolete.*

DISCLAIMER



SUMMARY

An analytical method has been developed for the determination of phenolic compounds in aviation fuels produced from coal-derived liquids. The method is based on gas chromatography/mass spectrometry (GC/MS) analysis of the sample and acquiring the data in the selected ion mode (SIM) of data acquisition. The calculation of the concentration of the phenolic species is performed with internal standard data. The internal standard approach was selected over external standard approaches because the former minimizes differences in injection of the sample onto the column. The method has a minimum detection limit of 0.01 weight percent or 100 ppm. The precision and accuracy of the method are acceptable, as defined by the evaluation criteria described for the analysis.

There are several limitations to this method. The major limitation is that absolute identification and concentration determination requires the availability of pure compounds. Pure compounds are needed to determine the retention times for confirmation of the identity of the species and to develop the sensitivity factors. When pure compounds are not available, the identification is only tentative and the concentration is estimated using an average sensitivity factor.

Another limitation of the method is that acquiring the data in the SIM mode of data acquisition does not provide all of the data potentially available from the sample. The SIM mode of acquisition acquires only the data for the ions selected for analysis of the compounds of interest (phenolic species). The mass spectral information for the remainder of the sample is lost. An additional analysis in the full-scan mode of data acquisition is required to provide this information. The additional analysis adds to the cost of the analysis and increases the turnaround time of the analysis.

Four product fuel samples produced by the Amoco Oil Company were analyzed by the method. The results from analysis of the three small-scale production samples indicated that concentration of individual phenolic species is below the detection limit of the method. This low level of phenolics in these samples probably will not have adverse effects on the stability of the fuels.

A C_3-substituted phenol was tentatively identified in the JP-8 fuel produced during the large-scale production experiment. The concentration of this species was extremely high relative to the concentrations determined in the small-scale production samples. This finding is believed to be in error because of possible interferences from tricycloalkanes present in the sample.

FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion and Power Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential for production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located near Beulah, North Dakota. Funding was provided to the Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the effort of the Western Research Institute (WRI), which, as a subcontractor to the University of North Dakota Energy and Minerals Research Center (UNDEMRC) (DOE contract number DE-AC22-87PC90016, UNDEMRC subcontract number 0213979) developed a method for the analysis of phenolic species in aviation fuels derived from coal liquids. DOE/PETC was funded through Military Interdepartmental Purchase Request (MIPR)-FY1455-86-NO657. Mr. William E. Harrison III was the Air Force Program Manager, Mr. Gary Stiegel was the DOE/PETC Program Manager, Dr. Curtis Knudson was the UNDEMRC Program Manager, and Mr. Edgar Smith was the WRI Program Manager.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SECTION I - INTRODUCTION

The Great Plains Gasification Plant (GPGP) near Beulah, North Dakota, produces about 145 MMscf/day of synthetic natural gas and three liquid by-product streams from pyrolysis of lignite coal. The three by-product streams--tar oil, crude phenol, and naphtha streams--have nominal production rates of 3,200, 915, and 725 barrels per stream day, respectively. For strategic reasons, the United States Air Force has been investigating the possibility of producing aviation turbine fuels from the three by-product streams. The Western Research Institute (WRI) has been involved in this study by performing laboratory hydrotreating studies of the by-product streams and evaluating of the products from these experiments. The research performed by WRI has demonstrated that aviation fuels can be produced from the by-product streams through hydrogenation processes (reference 1). Evaluation of the candidate fuels indicates that low levels of oxygen remain in the fuels after processing.

Lignite coal contains relatively high concentrations of oxygen, and the by-product streams, as expected, also contain high concentrations of oxygen. The three streams--tar oil, crude phenol, and naphtha streams--contain 2.70, 13.20 and 3.2 weight percent oxygen (dry basis), respectively. The oxygen-containing species in these streams are primarily in the form of phenolic compounds. The high concentration of oxygen species in these streams presents a problem for the production of aviation turbine fuels because these species must be removed to produce the finished fuels. As is often the case, the oxygen content is not reduced to zero during processing. The low concentration of oxygen remaining in the finished fuels may cause problems in meeting fuel specifications and in maintaining long-term storage stability.

The chemical forms and distribution of the oxygen remaining in the fuels is of interest for both fuel processing considerations and for evaluating potential end-use problems of the fuels. Knowledge of these species remaining in the fuels after hydrotreating is important for understanding problems associated with selection of hydrotreating catalysts and processing conditions. The chemical form of the oxygen remaining in the fuel may also have an effect on the fuel's stability and combustion properties. For these reasons, the identification and quantitative determination of the oxygenated species will assist in the evaluation of potential end-use problems of the fuels.

The research reported here was directed at developing an analytical method for the analysis of oxygenated species in aviation turbine fuels and the analysis of selected aviation turbine fuels produced from coal-derived liquids. The approach selected for this analysis is an internal standard method based on gas chromatography/mass spectrometry (GC/MS) and requiring data acquisition by selected ion monitoring (SIM). The decision to acquire the data by SIM was made to improve the signal-to-noise ratio of the method since the oxygenated species are present at trace concentrations. The use of SIM limits the qualitative power of GC/MS, and therefore selected compound classes must be targeted for analysis by the method. The phenolic species were targeted for analysis because they represent the most prominent class of oxygenated species in the by-product streams. The remainder of this report discusses the development of the analytical method, the limitations of the method, and the results of the analysis of selected coal-derived aviation fuel samples.

SECTION II - EXPERIMENTAL METHODS

The method developed for the analysis of oxygenated species in aviation fuels produced from coal liquids is based on analysis by GC/MS. This section describes the instrumental conditions used for the analysis and the procedures used for preparation of samples and standard solutions.

1. Qualitative Assessment

The by-product streams and selected, partially hydrogenated products were evaluated in a qualitative manner by GC/MS. The evaluation was performed on a Hewlett/Packard (HP) 5985B GC/MS system using the instrumental parameters provided in Table 1. The data were collected in the full-scan mode of data acquisition, and the mass spectra were evaluated to identify the individual species. The interpretation of the mass spectra was performed by evaluation of the fragmentation pattern, comparison of the mass spectra with mass spectra of pure compounds from the literature and internal libraries, and by co-injection of pure compounds.

2. Quantitative Determination

The method development and quantitative determinations were performed using the same instrumental parameters provided in Table 1 except the data were recorded in the selected ion monitoring (SIM) mode of acquisition. The selection of ions for

monitoring was based on the fragmentation pattern of the compounds targeted for analysis. The acquisition dwell time for these determinations was 100 milliseconds for each ion.

The sensitivity factors were calculated using the selected ion area responses from analysis of standard solutions. The equation defining the sensitivity factor is provided in Appendix A. The concentration of the targeted compounds was calculated from the sensitivity factors and the area response of the selected ions using another equation in Appendix A. The minimum detection limit (MDL), accuracy, and precision of the method were evaluated using the equations and discussion provided in Appendix B.

Table 1. Gas Chromatograph/Mass Spectrometer Conditions Used for the Qualitative Assessment of the By-Product Streams and Selected Hydrotreated Products

Gas Chromatograph	
Column	Carbowax 20M (25m x 0.20 mm [ID])
Carrier gas	Helium
Carrier flow rate	0.75 ml/min
Injection pressure	15 psig
Injection temperature	250°C
Column oven program	
Initial temperature	50°C
Time 1	3.0 min
Rate	3.0°C/min
Final temperature	200°C
Time 2	20 min
Mass Spectrometer	
Ionization mode	Electron impact
Ionization voltage	70 v
Ion source temperature	200°C
Electron multiplier voltage	1600 v
Data acquisition mode	Full scan
Mass range scanned	50-500 amu
Analysis duration	70 min

3. Sample and Standard Solution Preparation

The samples were prepared on a weight percentage basis by adding a known quantity of 2-chloronaphthalene (internal standard) to a known quantity of the sample at approximately the 0.05 weight

percent level. The samples were sealed in septum closure vials and refrigerated until analyzed.

The standard solutions were also prepared on a weight percentage basis. A stock solution was prepared at the 1 weight percent level of each of the targeted compounds in toluene. Standard solutions covering the range of 0.25 to 0.001 weight percent were prepared by serial dilution of the stock solution with toluene. The standard solutions were prepared for analysis using the same procedure described above for preparation of the samples.

SECTION III - RESULTS AND DISCUSSION

Two general approaches can be followed in developing an analytical method for the analysis of trace quantities in unknown samples: (1) a method that is universally general and relies on a complete qualitative evaluation of each unknown sample to determine what species will be analyzed, and (2) a method that is specific for selected compounds or compound types that are targeted for analysis. Both approaches have strong and weak points that must be considered in developing an analytical method.

We selected the latter approach for the following reasons:

1. All of the aviation fuel samples to be analyzed by the method will be of a similar nature and should contain the same classes of oxygenated species.

2. The cost of analysis can be reduced if each sample does not have to be evaluated before the analysis is performed.

3. Lower detection limits can be established for the method if selected compounds are targeted for the analysis.

The development of the method was divided into several tasks. The tasks were designed to address problems such as identifying the types of oxygenated species present in the fuel samples and determining their approximate concentrations. The tasks that were identified include (1) optimization of the gas chromatographic conditions, (2) evaluation of the by-product streams and partially hydrogenated products, (3) development of sensitivity factors, and (4) evaluation of the minimum detection limit, accuracy, and precision of the method. The approach to addressing these tasks and the results from their completion will be discussed in this section.

1. Optimization of Gas Chromatographic Conditions

The initial effort for development of the method was to determine the optimum gas chromatographic conditions for the separation of oxygenated species. This is a necessary first step because optimum separation is required for identification of individual species and to minimize interferences in the determinations. The parameters evaluated for this task included column material, carrier gas flow rate, and column oven temperature program. A sample of the crude phenol stream was used for optimization of the separation because this stream has the highest concentration of oxygen based on elemental analysis. Conditions found to separate the wide diversity of compounds in this stream are felt to be sufficient to separate the oxygenated species present in the remaining streams.

Two major factors were considered in the definition of the optimum conditions: maximum separation of the individual species and minimum analysis time. The results of this task were the gas chromatographic conditions provided in Table 1. These conditions provide good resolution among the species identified in the sample of the crude phenol stream and the analysis time is about 1 hour.

2. Qualitative Evaluation of the GPGP By-Product Streams

Samples of the crude phenol and tar oil streams were evaluated by GC/MS using the conditions provided in Table 1. These streams were evaluated to understand the types of oxygenated species present and not to identify the individual components. This level of effort was selected because the evaluation is only a screening exercise to identify the classes of oxygenated species present.

The effort was limited to the identification of the compound classes and not the individual species because of the difficulty in identifying many of the individual compounds by interpretation of their mass spectra. The difficulty in identifying individual compounds based on the fragmentation pattern is demonstrated by Figure 1, which presents the mass spectra of 2-ethylphenol and 3-ethylphenol. The close similarity of the two mass spectra makes it impossible to distinguish between the two compounds based only on the mass spectra. The two compounds can be identified by using other

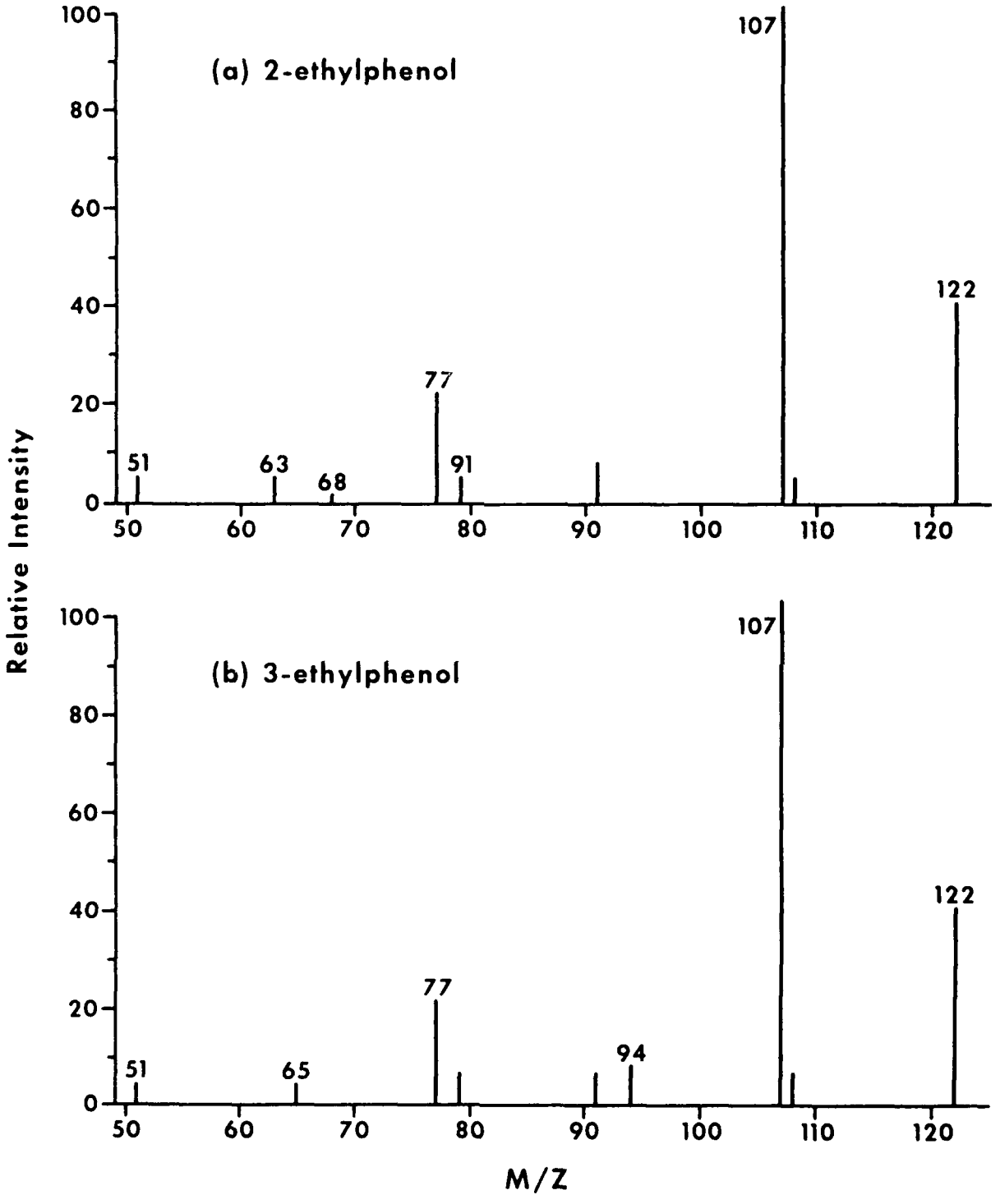


Figure 1. Mass Spectra of 2-Ethylphenol and 3-Ethylphenol

Table 2. Composition of the Crude Phenol Stream as Determined by GC/MS Analysis

Compound or Compound Class	Mass	Relative Area Percent
Toluene	92	0.1
C_2-benzene[1]	106	0.1
Phenol	94	23.2
C_1-phenol	108	9.1
C_1-phenol	108	12.7
C_1-phenol	108	13.7
C_2-phenol	122	0.6
C_2-phenol	122	1.2
C_2-phenol	122	6.0
C_2-phenol	122	1.1
Naphthalene	128	2.2
C_2-phenol	122	3.7
C_2-phenol	122	0.9
C_2-dihydroxy benzene	138	1.1
Catechol	110	1.5
C_2-phenol	122	1.7
C_3-phenol	136	0.1
C_3-phenol	136	0.4
C_3-phenol	136	0.2
C_3-phenol	136	0.5
C_3-phenol	136	0.3
C_3-phenol	136	2.6
C_1-dihydroxy benzene	124	2.4
C_3-phenol	136	0.2
C_3-phenol	136	0.2
C_3-dihydroxy benzene	152	0.5
Guaiacol	124	4.3
C_4-benzene	134	0.4
C_3-phenol	136	0.4
C_3-phenol	136	0.1
C_4-benzene	134	1.0
C_2-dihydroxy benzene	138	0.7
C_2-dihydroxy benzene	138	2.0
C_2-dihydroxy benzene	138	0.2
C_2-dihydroxy benzene	138	0.2
C_2-dihydroxy benzene	138	0.4
C_2-dihydroxy benzene	138	2.5
Hydroxy tetralin	148	0.2
C_2-dihydroxy benzene	138	0.2
C_2-dihydroxy benzene	138	0.2

Table 2. Composition of the Crude Phenol Stream as Determined by GC/MS Analysis (continued)

Compound or Compound Class	Mass	Relative Area Percent
C_3-dihydroxy benzene	152	0.2
C_3-dihydroxy benzene	152	0.5
C_3-indan/C_2-tetralin	146	0.4
C_3-dihydroxy benzene	152	0.2
Hydroxynaphthalene	144	0.2
Hydroxynaphthalene	144	1.7
C_1-hydroxynaphthalene	158	0.1
C_1-hydroxynaphthalene	158	0.1
C_1-hydroxynaphthalene	158	0.2

1 The subscript indicates the number of carbon atoms in the alkyl substituents.

Table 3. Phenolic Species Identified in the Tar Oil Stream by GC/MS Analysis

Compound or Compound Class	Mass	Relative Area Percent
C_2-phenol[1]	122	0.1
Phenol	94	2.9
C_1-phenol	108	2.3
C_1-phenol	108	0.5
C_1-phenol	108	2.3
C_2-phenol	122	2.4
C_2-phenol	122	0.1
C_2-phenol	122	6.8
C_2-phenol	122	1.8
C_2-phenol	122	3.5
C_3-phenol	136	1.8
C_4-phenol	150	0.1
C_3-phenol	136	1.0
C_4-phenol	150	0.3
C_3-phenol	136	0.7
C_4-phenol	150	0.7

1 The subscript indicates the number of carbon atoms in the alkyl substituents.

data, such as a comparison of gas chromatographic retention times with the retention times of known compounds, or by conducting co-injection experiments. Both of these require levels of effort above what is required for the screening nature of this task.

The naphtha stream was not evaluated during this task because its distillation range is below the range acceptable for aviation fuels (reference 1). For this reason, this stream is not of economic importance to the production of aviation fuels from the coal-derived liquids.

The results of the analysis of the crude phenol stream are listed in Table 2. The results are presented as the number of alkyl substitutes on the major functionality or structure. For example, the designation of C_2-phenol in the table indicates a phenolic species containing two carbon atoms as alkyl substituent(s). The exact structure could be dimethyl or ethyl substituted. The distinction between the two structures was not made for the reasons discussed previously. The concentration of each species is estimated as the area percentage of the total ion current of the compound relative to the total ionization of the chromatogram.

Examination of the results (Table 2) indicates that the major class of oxygenated species in the crude phenol stream is alkyl phenols. The other two classes of oxygenated species are the dihydroxy benzenes and the hydroxy naphthalenes. Other oxygenated species such as furans were not detected in the sample. Traces of aromatic hydrocarbons were also detected.

The results of the qualitative evaluation of the tar oil stream are listed in Table 3. Only the oxygenated species detected in the sample are listed because of the complexity of the sample. The major class of oxygenated compounds detected in the tar oil stream sample is alkyl phenols. Smith (reference 1) reported that additional oxygenated species were identified in the tar oil, but the evaluation reported by Smith was performed on chromatographically generated fractions and not the total stream. The chromatographic separation simplifies and concentrates the sample, which allows identification of species not detectable in the whole sample.

The evaluation of the crude phenol and tar oil streams shows that the alkyl phenols are the most predominate class of oxygenated compounds in these samples. This is interpreted as an indication that the trace levels of oxygenated species in finished aviation turbine fuels will probably be phenols.

Selected hydrotreated products from the crude phenol and tar oil streams were analyzed to confirm this indication.

3. Qualitative Evaluation of WRI-Produced Fuels

The evaluation of the by-product streams indicated that phenolic species represent the major fraction of the oxygenated compounds in these streams. Three hydrotreated products from the hydrotreating studies conducted by WRI were selected for evaluation to confirm that the phenolic species are the major class of oxygenated species occurring in the finished fuels and to determine which species tend to survive the hydrotreating process (reference 1). Two fuels with significantly different oxygen contents produced by hydrotreating the crude phenol stream (87-07-1 and 87-07-10) and one fuel produced by hydrotreating the tar oil stream (87-09-7) were selected for this evaluation. The hydrotreating conditions employed to produce these three samples are provided in Table 4. The experimental methods and the complete results for the experiments used to produce these samples have been discussed by Smith (reference 1). The elemental compositions of the three samples were determined and are provided in Table 5. The oxygen concentrations in these samples range from 12 to 0.6 weight percent.

The three samples were evaluated by interpretation of the full-scan acquired mass spectral data (Table 1). The raw data were interpreted to determine the class of compounds present in each sample based on the fragmentation pattern. The retention times of the unknown compounds were compared with retention times of known compounds in standard solutions. Tentative identifications were then made based on similarity of the fragmentation patterns and retention times.

The results of the evaluation of the three samples are summarized in Table 6. These results indicate that the phenolic compounds are the oxygen-containing components in the samples. Further evaluation of the results shows that the majority of the phenolic species identified have alkyl substituents in the 2 and 6 positions.

Alkyl-substituted phenols with substitutions in the 2 and 6 positions are considered to be hindered phenols. That the hindered phenols tend to survive the hydrotreating process is not surprising. The alkyl substituents adjacent to the oxygen substitution will hinder the interaction between the phenolic -OH and the active site on the catalyst. This interference between the molecule and the catalyst will allow the hindered phenols to survive the hydrotreating process.

Table 4. Hydrotreating Conditions Used to Produce the Fuel Samples Used to Evaluate the Oxygenated Compounds

Hydrotreating Condition	Fuel Sample from Phenols Stream		Fuel Sample from Tar Oil Stream
	87-07-1	87-07-10	87-09-7
Temperature:	550°F	590°F	575°F
LHSV:	1.0	1.0	0.5
Pressure:	2000 psig	2000 psig	2000 psig
H_2:	6000 SCFB	6000 SCFB	6000 SCFB
Catalyst	Shell 424	Shell 424	Shell 424

Table 5. Elemental Composition of WRI-Produced Fuel Samples Used to Evaluate Oxygenated Compounds, wt. %

Element	Fuel Samples from Phenols Stream		Fuel Samples from Tar Oil Stream
	87-07-1	87-07-10	87-09-7
C	77.8	85.9	86.5
H	9.2	14.4	10.7
N	0.5	0.1	0.5
S	0.2	<0.1	0.2
O	12.0	0.6	2.4

The results of the evaluation of the by-product streams and the WRI-produced aviation fuels show that the phenolic species are the major class of oxygenated species in the samples. In addition, the hindered phenolics survive the hydrotreating process. These results indicate that the analytical method should target the analysis of phenolic species. The following sections will discuss the development of the analytical method targeted for the analysis of phenols in aviation fuel samples.

Table 6. Oxygenated Species Identified in the WRI-Produced Fuel Samples

Compound or Compound Class	WRI Sample Number		
	87-07-1	87-07-10	87-09-7
Phenol	773	ND[1]	ND
2,6-dimethylphenol	835	858	849
2,4,6-trimethylphenol	935	920	938
2-methylphenol	974	954	962
2,3,6-trimethylphenol	975	997	988
C_3-phenol	1029	1001	ND
4-methylphenol	1084	ND	1093
2-ethylphenol and/or 2,5-dimethylphenol	1090	1113	1097
3-methylphenol	1093	ND	ND
2,4-dimethylphenol	1099	1122	1113
2,3-dimethylphenol	1188	1167	1177
C_3-phenol	1193	1249	1233
3,5-dimethylphenol	1224	ND	ND
C_3-phenol	1226	1247	1238
2,3,5,6-tetramethylphenol	1230	ND	ND
C_2-phenol	1233	ND	1241
2,3,4,6-tetramethylphenol	1244	ND	1254
C_3-phenol	1274	ND	1283
2,3,5-trimethylphenol	1281	1270	ND
C_4-phenol	1283	ND	ND
C_3-phenol	1295	ND	ND
C_4-phenol	1298	ND	ND
C_4-phenol	1340	ND	1354
C_3-phenol	1346	1369	1358
2,3,4-trimethylphenol	1353	ND	ND
C_3-phenol	1377	ND	1381
C_3-phenol	1393	ND	1387
3,5-diethylphenol	1452	ND	ND

[1] not detected

4. Selection of the Analytical Approach

The preceding discussion indicates that the analytical method should be targeted for the analysis of alkyl-substituted phenols. This section discusses the selection of the method used to analyze the fuels produced from coal-derived liquids. The method of analysis chosen for this project was GC/MS analysis. This method was chosen because it is believed to

provide more information regarding the sample than other available methods and because the detection limits are comparable to most other instrumentation-based approaches.

The initial evaluation of the hydrotreated products has indicated that phenolic species are the predominate class of oxygenated compounds. The levels of the individual phenolic compounds anticipated in the fuel samples are low, and the method selected for the analysis should have a low minimum detection limit. Data acquisition by selected ion monitoring (SIM) was chosen for this analysis. Data acquisition by this technique is based on selecting a series of ions diagnostic or representative of the compounds to be analyzed. The mass spectrometer is then programmed to scan only the ions selected. The dwell time (time the computer spends sampling a single ion) for each ion can be set to maximize the signal-to-noise ratio. This lowers the minimum detection limit of the method. Multiple ions were selected for analysis of each compound because the use of multiple ions increases the size of the signal used to perform the calculation and improves the minimum detection limit, the precision, and the accuracy.

The procedure selected for analysis of phenols in aviation fuel samples was an internal standard method, which removes errors associated with differences in sample injection from one analysis to another. This improves the overall accuracy and precision. The following sections discuss the development of the the method.

5. Development of Sensitivity Factors

A sensitivity factor, which relates the area response of a compound to its concentration, is required to calculate the concentration of each compound in a sample. The sensitivity factors are calculated from the data collected during a standard solution analysis. The concentration and area data of each compound and the internal standard are required for the calculation. The equation and procedures for developing the sensitivity factors are provided in Appendix A. The standard solutions are prepared from pure compounds as described in the experimental section.

The results of the qualitative evaluation showed that alkyl phenols containing up to four carbon atoms in the alkyl substituents were present in the hydrotreated fuel samples. A list of 69 possible phenolic isomers containing up to four carbon atoms in the alkyl substituents is provided in Table B-1 of Appendix B. A survey of the phenolic isomers available in the WRI pure compound library was performed and a list of these

isomers is provided in Table 7. The list is extensive but does not include the complete list of possible isomers. Several chemical supply companies were contacted to determine if additional phenolic isomers could be purchased for the project. Unfortunately, the isomers available through commercial sources only duplicated the compounds available from the WRI library. This presented a problem for the development of the method, because each compound to be analyzed requires a sensitivity factor that is determined experimentally from analysis of a standard solution.

Table 7. Phenolic Compounds Available in the WRI Pure Compound Library

Compound	Formula Weight
Phenol	94
2-methylphenol	108
3-methylphenol	108
4-methylphenol	108
2-ethylphenol	122
3-ethylphenol	122
2,3-dimethylphenol	122
2,4-dimethylphenol	122
2,5-dimethylphenol	122
2,6-dimethylphenol	122
3,4-dimethylphenol	122
3,5-dimethylphenol	122
2,3,5-trimethylphenol	136
2,3,6-trimethylphenol	136
2,4,6-trimethylphenol	136
2-methoxy-4-methylphenol	138
3,5-diethylphenol	150
2-propyl-4-methylphenol	150
2,3,5,6-tetramethylphenol	150
2-phenylphenol	170
2,6-di-tert-butylphenol	206

The lack of pure compounds was addressed by first developing the sensitivity factors for the compounds that are available and then determining the factor's range of variance. An attempt was then made to estimate sensitivity factors for compounds not available in pure form. Table 8 lists the sensitivity factors determined for the compounds available at WRI. The listed sensitivity factors are the mean values determined from analysis

of standard solutions at three concentration levels. The individual sensitivity factors and retention scan numbers for each compound from the analysis at each concentration are provided as Tables B-2 and B-3, respectively, in Appendix B.

Table 8 also lists the mean retention scan number and the ions used for the analysis. In most cases, two ions were selected to analyze each compound. The selection of the ions was based on selecting ions that represented a large fraction of the total ionization for each compound.

Table 8. Summary of Sensitivity Factors for Phenolic Standards

Scan No.	Compound	Ions for Analysis	Mean Sensitivity	RSD[1]
1334	phenol	94	2.340	9.31
1334	2,4,6-trimethylphenol	121,136	0.685	4.38
1139	2,6-dimethylphenol	107,122	0.950	7.39
1350	2-methylphenol	107,108	1.408	3.41
1412	2,3,6-trimethylphenol	121,136	0.765	6.27
1497	2-ethylphenol	107,122	0.925	6.69
1498	4-methylphenol	107,108	0.355	14.14
1503	2,5-dimethylphenol	107,122	0.971	1.65
1508	3-methylphenol	107,108	0.663	13.85
1514	2,4-dimethylphenol	122,107	0.895	11.97
1641	2,3-dimethylphenol	107,122	0.893	1.36
1689	2,3,5,6-tetramethyl-phenol	135,150	0.866	4.64
1690	3,5-dimethylphenol	107,122	0.849	1.52
1707	3-ethylphenol	107,122	0.825	3.11
1711	2,3,4,6-tetramethyl-phenol	135,150	2.145	2.83
1773	3,4-dimethylphenol	122	1.910	4.56
1778	4-methyl-2-propylphenol	150	3.581	2.21
1795	2,3,5-trimethylphenol	121,136	0.728	0.91
1925	4-tertbutylphenol	107,135,150	0.451	11.54
2019	3,5-diethylphenol	121,135,150	0.815	22.79
2049	3,4,5-trimethylphenol	121,136	0.628	1.90

[1] RSD (Relative Standard Deviation) = $\frac{\text{Standard Deviation}}{\text{Arithmetic Mean}} \times 100.$

The variation in sensitivity factors for each compound was evaluated by calculating the relative standard deviation (RSD) of the mean sensitivity factor. This approach evaluates the experimental error associated with determination of the

sensitivity factors and provides criteria for acceptance of the sensitivity factors. The approach for determining the acceptance criteria for the sensitivity factors is based on methods adopted by the U. S. Environmental Protection Agency. The mean sensitivity factor is considered acceptable if the RSD is equal to or less than 20.0%.

Examination of the RSD values in Table 8 indicates that only the RSD for 3,5-diethylphenol fails to meet the acceptance criteria. The reason for this failure is evident from the data provided in Table B-2 (Appendix B). The concentration range used for this compound is lower than the ranges used for the other compounds. The lowest concentration used for determining the sensitivity factor for this compound is 0.01 weight percent. This concentration appears to be below the effective minimum detection limit for this compound, which results in a significant error in determining the sensitivity factor.

The sensitivity factors listed in Table 8 are applicable for determining the concentration of the compounds listed in the table. The problem remains for estimating the concentration of compounds present in the samples but not available in pure form. The approach selected for estimating the concentration of these compounds is to use the mean sensitivity factor of selected compounds listed in Table 8. The compounds selected for determining a mean sensitivity factor are (1) those compounds for which two ions were used to develop the sensitivity factor, and (2) compounds for which the sensitivity factors passed the acceptance criteria (RSD less than or equal to 20.0%). The mean sensitivity factor determined from the data in Table 8 is 0.909 (standard deviation = 0.395). The sensitivity factor of 0.909 will be used in this method for estimating the concentration of compounds present in a fuel sample but not available in pure form for experimentally determining a sensitivity factor.

6. Evaluation of the Method

The method was evaluated before it was applied to the analysis of aviation fuel samples. Three criteria were used to evaluate this method: (1) minimum detection limit, (2) accuracy, and (3) precision. The minimum detection limit (MDL) is defined as the lowest concentration for which accurate analyses can be performed. The accuracy of the method is the degree to which the method can determine the true value, and the precision is the repeatability of the method.

The MDL, accuracy, and precision were determined using standard solutions containing 3-methylphenol, 2-ethylphenol, 2,6-dimethylphenol, 2,3,6-trimethylphenol, and 2,3,5,6-

tetramethylphenol. These five compounds were selected for the evaluation because they represent the alkyl substituent carbon number range of the species identified in the WRI-produced fuels. A stock solution at the nominal 1 weight percent level of each component was prepared. Additional solutions to the 0.01 weight percent level were prepared by serial dilution. The solutions were analyzed using the conditions listed in Table 1 and the data acquired in the SIM mode. The data from these analyses were used to estimate the three parameters using the equations provided in Appendix C.

The equation used to estimate the MDL for this evaluation defines the lowest concentration level that can be accurately measured by the method. This detection limit differs from other definitions that estimate the lowest concentration that can be detected by a method. The former definition was selected for this method because detection of the response is not as important as measurement of the concentration. The definition selected for this method is directed at determining the lowest concentration level where reliable concentration measurements can be performed. The results of the evaluation of the MDL are provided in Table 9.

Table 9 lists the data defining the calibration curve (slope, intercept, and correlation coefficient), the average noise level surrounding the response, and the MDL for each compound. The first point to note from these results is the values of the correlation coefficients of the calibration curves. The values range from 0.993 to 0.999. This range indicates that the data for each compound can be described by a linear relationship. A perfect fit of the data would have a correlation coefficient of 1.0. Deviations from 1.0 indicate a deviation of the data from a linear relationship. The closeness of the correlation coefficients to 1.0 indicates a good linear approximation of the data. From an analytical perspective, the linear fit of the data indicates a linear response of the mass spectrometer and that a single sensitivity factor can be used to determine the concentration over the range from 0.01 to 1.0 weight percent.

The noise level used to determine the MDL is 3 (response units) for each of the compounds. This low level of noise was designed into the method by selection of the SIM mode of data acquisition and the use of multiple ions for the analysis. The MDL values range from 0.003 to 0.010 weight percent. The largest value, 0.010 weight percent (100 ppm), is the MDL for the method.

Table 9. Results of the Evaluation of the Minimum Detection Limit

Compound	Calibration Curve			Average Noise	MDL[1] (wt%)
	Slope	Intercept	Regression Coefficient		
3-Methylphenol	0.000057	0.0064	0.993	3	0.008
2-Ethylphenol	0.000074	0.0051	0.998	3	0.007
2,6-Dimethylphenol	0.000106	-0.0001	0.999	3	0.003
2,3,6-Trimethylphenol	0.000116	0.0060	0.998	3	0.001
2,3,5,6-Tetramethyl-phenol	0.000093	0.0000	0.999	3	0.003

[1] MDL = Minimum Detection Limit = a(X) + b
where a = slope of calibration curve
b = intercept of calibration curve
X = ten times the average noise level

The method accuracy was estimated by the analysis of an in-house reference standard containing the five compounds listed previously at a nominal concentration level of 0.065 weight percent. The accuracy is evaluated by calculating the percent bias (see Appendix C), which compares the concentration measured by the method to the expected concentration in a reference standard. Using the approach developed by the U. S. Environmental Protection Agency, the method has acceptable accuracy if the absolute value of the percent bias is less than or equal to 20%.

The results of the accuracy evaluation are provide in Table 10. Examination of these results indicate that the method has acceptable accuracy as defined by the percent bias. The values of the percent bias range from 8.6 to 11.3%, and all of the values are positive. The positive nature of the values indicates that the method will overestimate the concentration of the individual species.

The precision of the method was evaluated by split analyses of a standard solution containing the five previously listed compounds at the nominal 0.25 weight percent level. The split analyses were performed by first preparing two aliquots of the standard solution. The two aliquots were then analyzed using the conditions listed in Table 1 and by acquiring the data in the SIM mode. The precision was estimated by calculating the relative percent deviation (RPD) of the results from the two analyses (Appendix C). The U. S. Environmental Protection Agency criterion of acceptance (RPD less than or equal to 20%) was used to accept the precision of the method.

Table 10. Results of the Evaluation of the Accuracy of the Method

Compound	Concentration, wt%		Percent Bias[1]
	Expected	Measured	
3-Methylphenol	0.067	0.074	10.6
2-Ethylphenol	0.067	0.073	9.0
2,6-Dimethylphenol	0.065	0.070	8.8
2,3,6-Trimethylphenol	0.093	0.104	11.3
2,3,5,6-tetramethyl-phenol	0.066	0.072	8.6

[1] Percent Bias (%B) = $\frac{(C_m - C_e)}{C_e} \times 100$

The results of the precision evaluation are provided in Table 11, which shows the concentration determinations for the two analyses and the calculated RPD. All of the RPD values are acceptable because they are below the 20% acceptance level.

Table 11. Results of the Evaluation of the Precision of the Method

Compound	Concentration, wt%		RPD[1]
	Split 1	Split 2	
3-Methylphenol	0.258	0.268	4.0
2-Ethylphenol	0.316	0.279	12.4
2,6-Dimethylphenol	0.249	0.263	5.7
2,3,6-Trimethylphenol	0.371	0.379	2.1
2,3,5,6-Tetramethyl-phenol	0.260	0.268	2.9

[1] RPD (Relative Percent Deviation) = $\frac{(M_1 - M_2)}{(M_1 + M_2)/2} \times 100$

7. Method Procedures

The analytical method developed for the analysis of phenolic species in aviation fuels has been described and evaluated in the previous sections. This section will summarize the analytical procedure. The details of the method, including all data quality control procedures, are provided as Appendix D as a standard operating procedure.

The method is a GC/MS-based method for the collection of raw data in the SIM mode of data acquisition. The concentration of each species is determined as the weight percentage of the species in the sample. The results are calculated using the area responses of the compound and the internal standard (2-chloronaphthalene), the sensitivity factor of the compound and the concentration of the internal standard in the sample. Data quality is insured by tuning and calibration of the GC/MS system and through evaluation of reference standard samples and split analyses.

8. Method Application and Limitations

The method discussed in the previous sections is applicable to the analysis of phenolic species in a hydrocarbon-based matrix.

The method is capable of analyzing individual phenolic compounds to a level of 0.01 weight percent or 100 ppm.

There are several limitations to this method. The major limitation is that absolute identification and concentration determination requires the availability of pure compounds. Pure compounds are needed to determine the retention times for confirmation of the identity of the species and to develop the sensitivity factors. When pure compounds are not available, the identification is only tentative and the concentration is estimated using an average sensitivity factor.

Another limitation of the method is that acquiring the data in the SIM mode does not provide all of the data potentially available for the sample. The SIM mode only acquires data for ions selected of the compounds of interest (phenolic species). The mass spectral information for the remainder of the sample is lost. An additional analysis in the full-scan mode of data acquisition is required to provide this information. The additional analysis adds to the cost and increases the turnaround time of the analysis.

SECTION IV - ANALYSIS OF SELECTED FUEL SAMPLES

Four samples were received from the Amoco Oil Company for analysis to determine the level of oxygenated compounds in each sample. Three of the samples were produced from the small-scale production studies and represent a JP-4, a JP-8, and a JP-8X fuel, respectively; the fourth sample was a JP-8 produced from the large-scale production test (reference 2).

The four samples were analyzed for phenolic compounds using the method discussed previously, and the results are provided in Table 12. Three phenolic species were identified among the four samples. The three species were not available in the WRI pure compound library, and an absolute identification could not be made. Each of the three species contained three carbon atoms in the alkyl substituents and are identified in Table 12 as C_3-Phenol-a, C_3-Phenol-b, and C_3-Phenol-c.

The concentrations of the phenolic species in the JP-4 and JP-8 fuels produced from the small-scale tests are below the detection limit of the method. The calculated values are reported in the table to demonstrate that the compounds were detected even though the accuracy of the values may be in question because the concentrations are below the minimum detection limit.

Table 12. Results of the Phenolics Analysis of the Amoco-Produced Fuel Samples

Compound	Concentration, wt%			
	Small-Scale Samples			
	JP-4	JP-8	JP-8X	JP-8
C_3-Phenol-a	N.D.[1]	0.006	0.028	0.124
C_3-Phenol-b	N.D.	0.001	0.023	N.D.
C_3-Phenol-c	0.001	0.002	0.005	N.D.

[1] N.D. is Not Detected

The concentration of the C_3-Phenol-a in the large-scale-produced JP-8 fuel may be in question. Tricycloalkanes produce fragment ions during electron impact mass spectrometry that have the same mass-to-charge ratios as do those produced from several of the phenolic species. The production of common ions from two classes of compounds provides the opportunity for interference in the analysis. The relatively high concentration of the C_3-Phenol-a as compared with its concentration in the other samples indicates that there may be an error in the determination.

SECTION V - CONCLUSIONS

An analytical method has been developed for the determination of phenolic compounds in aviation fuels produced from coal-derived liquids. The method is based on GC/MS analysis of the sample and acquiring the data in the selected ion mode. The concentration of the phenolic species is calculated with internal standard data. The internal standard approach was selected over external standard approaches because the former minimizes differences in injection of the sample onto the column. The method has a minimum detection limit of 0.01 weight percent or 100 ppm. The precision and accuracy of the method are acceptable, as defined by the evaluation criteria described for the analysis.

There are several limitations to this method. The major limitation is that absolute identification and concentration determination requires the availability of pure compounds, which are needed to determine the retention times for confirmation of the identity of the species and to develop the sensitivity

factors. When pure compounds are not available, the identification is only tentative and the concentration is estimated using an average sensitivity factor.

Another limitation is that acquiring the data in the SIM mode does not provide all of the data potentially available for the sample. The SIM mode acquires data only for selected ions of the compounds of interest (phenolic species). The mass spectral information for the remainder of the sample is lost. An additional analysis in the full-scan mode is required to provide this information. The additional analysis adds to the cost for the analysis and increases the turnaround time of the analysis.

Four product fuel samples produced by the Amoco Oil Company were analyzed by this method. Analyses of the three small-scale production samples indicate that the concentration of individual that phenolic species is below the detection limit of the method. This low level of phenolics probably will not have adverse effects on the stability of the fuels.

A C_3-substituted phenol was tentatively identified in the JP-8 fuel produced during the large-scale production experiment. The concentration of this species was extremely high relative to the concentrations determined in the small-scale production samples. This result is believed to be in error because of possible interferences from tricycloalkanes in the sample.

REFERENCES

1. Smith, E. B., F. D. Guffey, and L. G. Nickerson, "Production of Jet Fuels from Coal-derived Liquids, Vol. III, Jet Fuel Potential of Liquid By-Products from the Great Plains Gasification Project," AFWAL-TR-87-2042, May 1988.

2. Furlong, Mark, Joe Fox, and Joe Masin, "Production of Jet Fuels from Coal-derived Liquids, Vol. IX, Results of Bench-Scale and Pilot Plant Testing," AFWAL-TR-87-2042, June 1989.

APPENDIX A

Equations For Calculating Sensitivity Factors and Concentration

The sensitivity factor and the concentration of each target compound were calculated on a Hewlett-Packard series 1000E computer, which functions as the data acquisition and processing computer for the GC/MS system used for this analysis. The software to perform these calculations was developed in-house specifically for this type of analysis. The software integrates the selected ion peak areas for each target compound, performs the calculation to obtain the sensitivity value for each target compound from an analysis of a standard solution, and calculates the concentration of each target compound from an analysis of an unknown sample or an in-house reference standard. The sensitivity for each selected compound is calculated using the following equation:

$$S = \frac{C_x}{I_x} \times \frac{I_s}{C_s}$$

where: S = sensitivity of selected compound
C_x = concentration of the selected compound
I_x = area of ion(s) selected for analysis
I_s = area of M/Z = 162 from 2-chloronaphthalene
C_s = concentration of 2-chloronaphthalene

The concentration of each selected compound in the samples submitted for analysis or in an in-house reference standard is calculated as the weight percentage of that compound in the sample. The concentration is calculated as the weight percentage using the following equation:

$$C_x = (C_s)\ (S)\ \frac{I_x}{I_s}$$

where: C_x = concentration of the selected compound
S = sensitivity of selected compound
C_s = concentration of 2-chloronaphthalene
I_x = area of ion(s) selected for analysis
I_s = area of M/Z = 162 from 2-chloronaphthalene

APPENDIX B

Raw Sensitivity Factor and Retention Scan Data

Table B-1. List of Possible Phenolic Compounds Having Up To Four Carbons in the Alkyl Substituents

Compound	Formula Weight	Available at WRI
Phenol	94	Y
2-methylphenol	108	Y
3-methylphenol	108	Y
4-methylphenol	108	Y
1,2-dihydroxybenzene (Catechol)	110	Y
1,3-dihydroxybenzene (Resorcinol)	110	Y
1,4-dihydroxybenzene (Hydroquinone)	110	N
2-ethylphenol	122	Y
3-ethylphenol	122	Y
2,3-dimethylphenol	122	Y
2,4-dimethylphenol	122	Y
2,5-dimethylphenol	122	Y
2,6-dimethylphenol	122	Y
3,4-dimethylphenol	122	Y
3,5-dimethylphenol	122	Y
2-methoxyphenol (Guaiacol)	124	Y
2,3,4-trimethylphenol	136	N
2,3,5-trimethylphenol	136	Y
2,3,6-trimethylphenol	136	Y
3,4,5-trimethylphenol	136	N
2,4,6-trimethylphenol	136	Y
2,4,5-trimethylphenol	136	N
2-ethyl-3-methylphenol	136	N
2-ethyl-4-methylphenol	136	N
2-ethyl-5-methylphenol	136	N
2-ethyl-6-methylphenol	136	N
2-methyl-3-ethylphenol	136	N
2-methyl-4-ethylphenol	136	N
2-methyl-5-ethylphenol	136	N
3-ethyl-4-methylphenol	136	N
3-ethyl-5-methylphenol	136	N
3-methyl-4-ethylphenol	136	N
2-n-propylphenol	136	N

Table B-1. List of Possible Phenolic Compounds Having Up To Four Carbons in the Alkyl Substituents (continued)

Compound	Formula Weight	Available at WRI
3-n-propylphenol	136	N
4-n-propylphenol	136	N
2-isopropylphenol	136	N
3-isopropylphenol	136	N
4-isopropylphenol	136	N
2-methoxy-4-methylphenol	138	Y
2,4-diethylphenol	150	N
2,5-diethylphenol	150	N
2,3-diethylphenol	150	N
2,6-diethylphenol	150	N
3,5-diethylphenol	150	Y
3,4-diethylphenol	150	N
2-propyl-3-methylphenol	150	N
2-propyl-4-methylphenol	150	Y
2-propyl-5-methylphenol	150	N
2-propyl-6-methylphenol	150	N
2-methyl-3-propylphenol	150	N
2-methyl-4-propylphenol	150	N
2-methyl-5-propylphenol	150	N
3-propyl-4-methylphenol	150	N
3-propyl-5-methylphenol	150	N
3-methyl-4-propylphenol	150	N
2-n-butylphenol	150	N
3-n-butylphenol	150	N
4-n-butylphenol	150	N
2-tert-butylphenol	150	N
3-tert-butylphenol	150	N
4-tert-butylphenol	150	N
2-sec-butylphenol	150	N
3-sec-butylphenol	150	N
4-sec-butylphenol	150	N
2,3,4,5-tetramethylphenol	150	N
2,3,5,6-tetramethylphenol	150	Y
2,3,4,6-tetramethylphenol	150	N
2-phenylphenol	170	Y
2,6-di-tert-butylphenol	206	Y

Table B-2. Raw Sensitivity Factor Data for the Phenolic Standards

Mean Scan	Compound	Ions for Analysis	Sensitivities 0.5%	0.1%	0.05%	0.01	Mean	RSD[1]
1139	2,6-dimethylphenol	107,122	1.011	0.874	0.966		0.950	7.39
1334	phenol	94	2.576	2.298	2.147		2.340	9.31
1334	2,4,6-trimethylphenol	121,136	0.667	0.715	0.673		0.685	4.38
1350	2-methylphenol	107,108	1.458	1.362	1.404		1.408	3.41
1412	2,3,6-trimethylphenol	121,136	0.798	0.710	0.787		0.765	6.27
1497	2-ethylphenol	107,122	0.888	1.000	0.887		0.925	7.02
1508	3-methylphenol	107,108	0.699	0.559	0.732		0.663	13.85
1514	2,4-dimethylphenol	122,107	0.992	0.913	0.780		0.895	11.97
1641	2,3-dimethylphenol	107,122	0.882	0.906	0.891		0.893	1.36
1689	2,3,5,6-tetramethyl-phenol	135,150	0.844	0.912	0.841		0.866	4.64
1690	3,5-dimethylphenol	107,122	0.858	0.854	0.834		0.849	1.52
1707	3-ethylphenol	107,122	0.832	0.797	0.847		0.825	3.11
1711	2,3,4,6-tetramethyl-phenol	135,150	2.214	2.100	2.121		2.145	2.83
1773	3,4-dimethylphenol	122	1.990	1.922	1.817		1.910	4.56
1778	4-methyl-2-propylphenol	150	3.672	3.544	3.527		3.581	2.21
1795	2,3,5-trimethylphenol	121,136	0.721	0.734	0.730		0.728	0.91
1925	4-tertbutylphenol	107,135,150	0.449	0.400	0.504		0.451	11.54
2019	3,5-diethylphenol	121,135,150		0.648	0.782	1.015	0.815	22.79
2049	3,4,5-trimethylphenol	121,136	0.618	0.624	0.641		0.628	1.90

[1] RSD (Relative Standard Deviation) = $\frac{\text{Standard Deviation}}{\text{Arithmetic Mean}} \times 100.$

Table B-3. Raw Scan Retention Data for the Phenolic Standards

Compound	Ions for Analysis	Retention Scan Number			
		Injection Number			
		1	2	3	Mean
phenol	94	1332	1335	1334	1334
2,4,6-trimethylphenol	121,136	1335	1335	1333	1334
2,6-dimethylphenol	107,122	1138	1139	1140	1139
2-methylphenol	107,108	1349	1350	1350	1350
2,3,6-trimethylphenol	121,136	1412	1412	1412	1412
2-ethylphenol	107,122	1496	1497	1498	1497
4-methylphenol	107,108	1496	1501	1498	1498
2,5-dimethylphenol	107,122	1503	1504	1503	1503
3-methylphenol	107,108	1506	1509	1510	1508
2,4-dimethylphenol	122,107	1514	1516	1513	1514
2,3-dimethylphenol	107,122	1641	1642	1641	1641
2,3,5,6-tetramethyl-phenol	135,150	1689	1688	1689	1689
3,5-dimethylphenol	107,122	1691	1689	1691	1690
3-ethylphenol	107,122	1707	1708	1707	1707
2,3,4,6-tetramethyl-phenol	135,150	1711	1712	1709	1711
3,4-dimethylphenol	122	1774	1773	1773	1773
4-methyl-2-propylphenol	150	1779	1778	1778	1778
2,3,5-trimethylphenol	121,136	1796	1796	1794	1795
4-tertbutylphenol	107,135,150	1926	1924	1925	1925
3,5-diethylphenol	121,135,150	2020	2018	2019	2019
3,4,5-trimethylphenol	121,136	2051	2047	2050	2049

APPENDIX C

Procedures For Estimating Minimum Detection Limit, Accuracy, and Precision

This appendix describes the specific procedures used to evaluate the method detection limit, accuracy, and precision of the method. The evaluation procedures described in this section are typical of those used to evaluate methods of this type. The procedures and equations that were used to perform the evaluations are provided below.

Minimum Detection Limit

The definition of the minimum detection limit (MDL) for this method includes consideration of the signal-to-noise ratio of the instrument and the ion area response size that minimizes integration errors. The MDL evaluation was performed by analyzing a series of samples of differing concentration and developing a calibration curve using linear regression methods. The MDL was then calculated from the linear calibration equation using an area response equal to 10 times the average background noise level adjacent to the target compound response. The equation provided below describes this calculation.

$$MDL = a(X) + b$$

where: MDL = minimum detection limit
a = slope of the calibration expression
b = intercept of the calibration expression
X = ten times the average background noise

The minimum detection limit is expressed as the minimum weight percentage of the particular compound that can be accurately detected and determined by the method.

Accuracy

Accuracy was estimated by percent bias in the analysis of standard solutions. The following equation was used to perform the evaluation.

$$B = 100 \times (C_m - C_t)/C_t$$

where: B = percent bias
C_m = measured concentration of standard reference material
C_t = actual concentration for standard reference material

The acceptance criteria for accuracy of the method is a percent bias less than 20%.

Precision

Precision was estimated by split analyses of standard solutions using the following equation:

$$RPD = \frac{(C_1 - C_2) \times 100}{(C_1 + C_2)/2}$$

where: RPD = relative percent difference
C_1 = the larger of the two observed values
C_2 = the smaller of the two observed values

Acceptable precision is defined by relative percent deviations less than 20%.

APPENDIX D

Standard Operating Procedure

I. Method Summary

This method is a procedure for the analysis of phenolic compounds suspected to be present in a fuel sample. The method is an internal standard procedure for determining the concentration of each compound as the weight percent of the sample.

II. Apparatus and Materials

A. A gas chromatograph/mass spectrometer system based on quadrupole mass separation. The system should be equipped with a computer-based data acquisition and processing system and a split/splitless gas chromatograph injector.

B. 10 microliter syringe.

C. 2-chloronaphthalene (internal standard).

D. Samples of the phenolic compounds selected for analysis (99%+ purity or purity stated by manufacturer's analysis) for use in preparing standard solutions.

E. Toluene, reagent grade.

F. Septum closure vials.

III. Analytical Procedure

A. Prepare as a minimum three standard solutions of the phenolic compounds selected for analysis. The concentrations of the compounds in the standard solutions should cover the range of concentrations anticipated for the samples.

B. To a suitable size aliquot of the standard solution add 2-chloronaphthalene (internal standard) at a concentration level comparable to the concentration of the compounds in solution.

C. Tune the GC/MS system to manufacturer's specifications using procedures recommended by the manufacturer.

D. Optimize the GC/MS conditions to the conditions listed in Table 1.

E. Acquire the GC/MS data for each of the standard solutions in the SIM mode of acquisition.

F. From the data acquired for each standard solution, determine the following:

1. Compound scan retention number.
2. Sensitivity factor as defined by the following equation:

$$S = \frac{C_x}{I_x} \times \frac{I_s}{C_s}$$

where: S = sensitivity factor
C_x = concentration of the selected compound
I_x = area of ion(s) selected for analysis
I_s = area of M/Z = 162 from 2-chloronaphthalene
C_s = concentration of 2-chloronaphthalene

G. To an aliquot of the sample(s) add 2-chloronaphthalene at a concentration level comparable to that used in the standard solutions.

H. Acquire the GC/MS data for the sample(s) containing the 2-chloronaphthalene.

IV. Data Reduction and Calculation

A. Confirm the identity of the selected compounds in the sample(s) using the fragmentation pattern and retention time data generated with the standard solutions.

B. Integrate the ion areas of the ion(s) identified for analysis of each selected compound.

C. Calculate the concentration of each selected compound using the following equation:

$$C_x = (C_s)\ (S)\ \frac{I_x}{I_s}$$

where: C_x = concentration of the selected compound
S = sensitivity factor of the selected compound
C_s = concentration of 2-chloronaphthalene

I_x = area of ion(s) selected for analysis
I_s = area of M/Z = 162 from 2-chloronaphthalene

V. Data Quality Assurance

A. The sensitivity factors of the selected compounds will be determined initially and any time that the system has been determined to be out of control using as a minimum three concentration levels of each selected compound. The validity of the initial sensitivity factors will be determined as a function of the relative standard deviation of the sensitivity factors from the mean value as defined by the following equation:

$$\text{RSD (Relative Standard Deviation)} = \frac{\text{Standard Deviation}}{\text{Arithmetic Mean}} \times 100.$$

The percent deviation must be less than or equal to 20% for acceptance. The sensitivity factors for each of the selected compounds will be verified daily or once in every 10 analyses (whichever is more frequent) by analysis of a standard solution. The standard solution used for this verification will be the standard solution with the concentration of the selected compounds closest to the concentration of the compounds in the samples. The validity of the sensitivity factors for each selected compound will be demonstrated so that the relative percent deviation (RPD) of the measured value is 20% or less. The RPD will be calculated using the following equation:

$$\text{Relative Percent Deviation} = \frac{C_1 - C_2}{(C_1 + C_2)} \times 100$$

where: C_1 = the larger value
C_2 = the smaller value

B. Split analyses will be performed at a minimum of one in every 10 samples to evaluate the precision of the method. The RPD must be 20% or less. The RPD will be determined using the equation provided above (VI. A.).

C. Duplicate analyses will be performed when sufficient sample is submitted and duplicate analyses are requested.

D. The accuracy of the method will be verified by analysis of an in-house reference standard at frequency of at least once in every 10 samples. The in-house reference standard will be prepared in the same manner as the standard solutions. This solution will be prepared at the concentration levels approximating the concentration levels of phenolic compounds observed in the fuel samples. The accuracy will be evaluated as the percent bias for the analysis of the in-house reference standard. The percent bias is defined by the following equation:

$$\text{Percent Bias} = \frac{C_m - C_t}{C_t} \times 100$$

where: C_m = measured concentration of reference standard

C_t = actual concentration in reference standard

For the accuracy of the method to be satisfactory, the percent bias must be equal to or less than 20%.

E. If the data quality assurance criteria are not met then the method is considered out of control and all analyses will be stopped. Corrective action will be taken to identify and correct the problem. After the problem is corrected, the validity of the method will be demonstrated with the quality assurance parameters.

*U.S.Government Printing Office: 1990—748-056/24392